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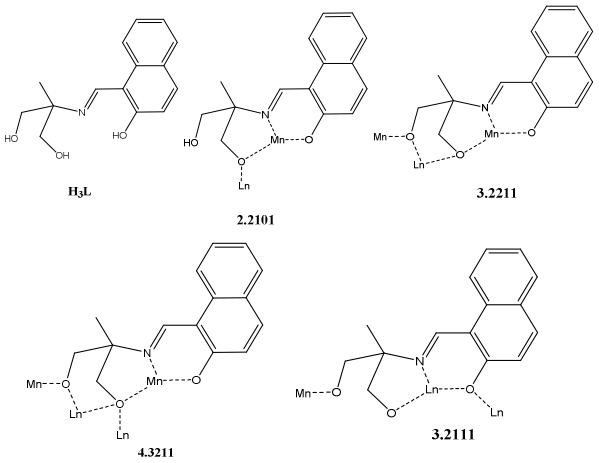
The use of H_3L (= 2-(β-naphthalideneamino)-2-hydroxymethyl-1-propanol) in mixed-metal manganese-lanthanide carboxylate cluster chemistry has led to the isolation of two new dodecametallic heteronuclear isostructural $[Mn^{III}_6Ln^{III}_6]$ complexes (Ln = Gd, Dy), with the Dy analogue displaying temperature and frequency dependent out-of-phase signals suggesting possible single molecule magnetism behaviour.

The rationalization of the magnetic properties in molecular clusters has been attracting the focus of the scientific community over the last few decades; discrete complexes or polymeric compounds have been found to function as magnetic species, retaining their magnetization below a critical/blocking temperature, thus paving the way for applications in magnetic data storage. The former, termed as Single Molecule Magnets (SMMs),[1] represent the lower limit in the size-scale of magnetic materials, while the latter, named as Single Chain Magnets (SCMs),[2] may be regarded as the one-dimensional analogues of SMMs. To further understand and elucidate the phenomena that govern the magnetic behavior of such species, more compounds have to be isolated and studied.

We had previously reported the use of the naphthalene-based triol ligand 2-(β-naphthalideneamino)-2-hydroxymethyl-1-propanol, H_3L (Scheme 1),[3] in Co(II/III), Ni(II) and Cu(II) chemistry,[4] while very recently we expanded our studies in mixed-metal Mn/Ln chemistry reporting on a family of octanuclear $[Mn^{III}_6Ln^{III}_2]$ complexes.[5] Herein, we move further in Mn/Ln/carboxylate cluster chemistry, and we present the synthesis, structures and magnetic properties of two mixed-metal dodecanuclear $[Mn^{III}_6Ln^{III}_6]$ clusters (Ln= Gd, Dy).



Scheme 1. The structure of H_3L and its coordination modes with corresponding Harris notation in **1** and **2**.

Reaction of $Mn(O_2CPh)_2{\cdot}2H_2O$, $Ln(NO_3)_3{\cdot}6H_2O$ (Ln = Gd, Dy) and H_3L in 1:1:1 ratio in the presence of base, NEt_3, afforded two new heterometallic dodecametallic clusters with the general formula $[Mn^{III}_6Ln^{III}_6(OH)_7(H_2O)_3(O_2CPh)_{11}(L)_3(HL)_4(NO_3)]{\cdot}6.5MeCN{\cdot}H_2O$ (Ln: Gd, **1**·6.5MeCN·H_2O; Dy, **2**·6.5MeCN·H_2O). The structure of **1** was solved by single-crystal X-ray crystallography, while complex **2** is proposed to be isostructural with **1** based on elemental analyses, IR spectra and powder XRD patterns (Figs S1 and S2). Cluster **1** crystallizes in the triclinic P-1 space group (Figure 1, top); its magnetic core (Figure 1, bottom) consists of a central Gd^{III} ion (Gd1) which forms a $[Gd_3Mn(OH)_3(OR)]$ cubane-like unit with Gd3, Gd2 and Mn1 *via* three μ_3-OH^- and one μ_3-OR^- groups. In addition, Gd1 participates in the formation of two defective cubanes; one consisting of Gd1, Gd5 and Mn3 *via* two μ_3-OH^-, one monoatomic μ-O_{NO3} and one μ-OR^- bridges; and one consisting of Gd1, Gd4 and Mn2 held *via* three μ_3-OH^- and one μ-OR^- groups and one additional μ-H_2O molecule. Furthermore, on each of these three cubane units, smaller metallic fragments are attached; more specifically, on each of Gd2 and Gd4, a trivalent Mn center is attached *via* two μ-OR^-

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bridges, while a quite rare 4.221 (Harris Notation)[6] nitrate anion is responsible for the bridging of the dimetallic {MnGd(O_R)$_2$} unit containing Mn5 and Gd6 to Gd3 and Mn3. From the seven ligands present, three are fully deprotonated, L^{3-}, while the remaining four are doubly deprotonated, HL^{2-}. Concerning the three fully deprotonated ligands, one adopts the 3.2211 coordination mode, one is in the 4.3211 mode and the last assumes the 3.2111 mode. All four of the doubly deprotonated ligands adopt the 2.2101 binding fashion. From the eleven benzoate molecules present in the structure, eight are found in the usual *syn-syn* – η^1: η^1: μ mode, while the remaining three coordinate in a terminal monodentate fashion. Finally, the coordination environment is completed by the presence of two terminally bound water molecules. All manganese centers are in the 3+ oxidation state as confirmed by bond-valence sum calculations[7] (BVS values: 3.10, 3.02, 3.17, 3.00, 3.15 and 3.22, for Mn1, Mn2, Mn3, Mn4, Mn5 and Mn6, respectively), with Mn1, Mn2 and Mn3 being six-coordinate adopting a *Jahn-Teller* distorted octahedral geometry, while Mn4, Mn5 and Mn6 are five-coordinate adopting a square pyramidal geometry (τ values[8] of 3.53, 2.40 and 1.32 for Mn4, Mn5 and Mn6, respectively).

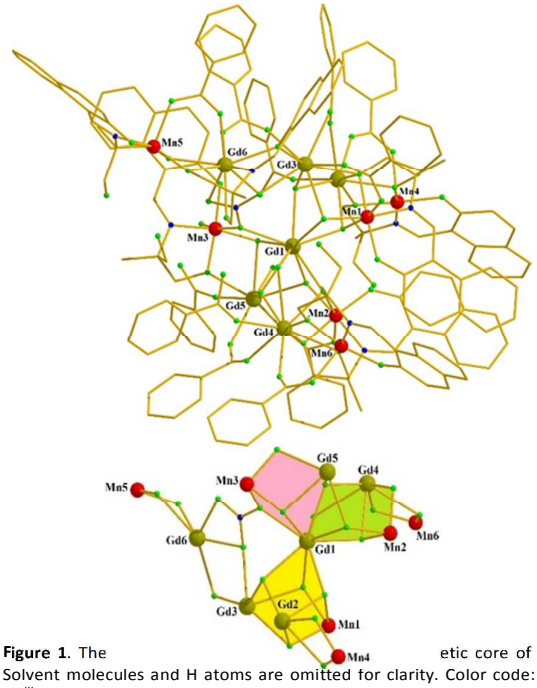


Figure 1. The etic core of **1** (bottom). Solvent molecules and H atoms are omitted for clarity. Color code: Mn^{III} = red, Gd^{III} = dark-yellow, O = green, N = blue, C = grey.

Using SHAPE-analysis,[9] the lanthanide centers can be divided in to four categories with respect to their geometry (Figure 2): i) Gd1 and Gd4 are nine-coordinate adopting spherical capped square antiprismatic geometry, ii) Gd2 is eight-coordinate with a triangular dodecahedral geometry, iii) Gd3 and Gd5 are eight-coordinate adopting square antiprismatic geometry, and iv) Gd6 is nine-coordinate with a capped square antiprismatic geometry.

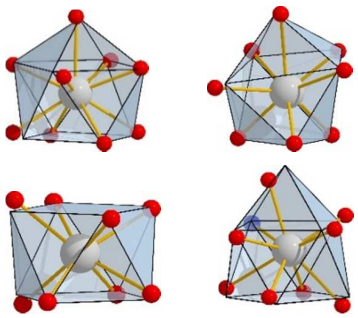
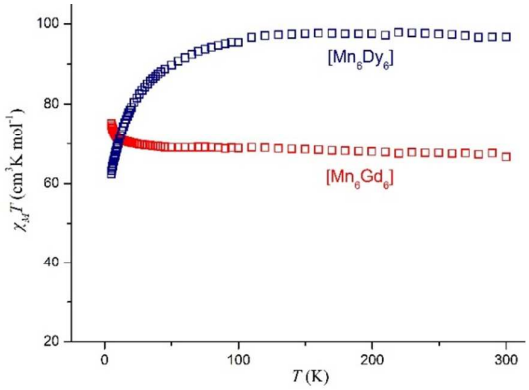


Figure 2. The coordination polyhedra for the lanthanide centers present in **1**; Gd1 and Gd4 (top-left), Gd2 (top-right), Gd3 and Gd5 (bottom-left) and Gd6 (bottom-right).

Variable temperature dc magnetic susceptibility data was collected for both complexes in the temperature range 5-300 K under an applied field of 0.1 T. These are plotted as $\chi_M T$ versus T plots in Figure 3. For **1**, the room temperature $\chi_M T$ value of 66.65 cm^3 K mol^{-1} is very close to the expected value of 65.25 cm^3 K mol^{-1} for six non-interacting Mn^{III} (with g = 2.0) and six-non interacting Gd^{III} ions (g = 2.00). Upon cooling the value of $\chi_M T$ increases slightly until ~15 K, below which it increases to a maximum value of 76.81 cm^3 K mol^{-1} at 5 K. For **2**, the room temperature $\chi_M T$ value of 96.72 cm^3 K mol^{-1} is slightly lower than the expected value of 102.57 cm^3 K mol^{-1} for six non-interacting Mn^{III} (with g = 2.0) and six-non interacting Dy^{III} ions (S = 5/2, L = 5, J = 15/2, g_j = 4/3). Upon cooling the value of $\chi_M T$ remains fairly constant until ~100 K, below which it decreases to a final value of 62.38 cm^3 K mol^{-1} at 5 K.

Figure 3. $\chi_M T$ *vs.* T plot for complexes **1** ([Mn_6Gd_6]) and **2** ([Mn_6Dy_6]) under an applied *dc* field of 0.1 T.



closer inspection of the two structures reveals that there are no bridges between Mn pairs with three or less bridging atoms, therefore suggesting that for **1** magnetic behavior mainly results from the Mn^{III}-Gd^{III} and Gd^{III}-Gd^{III} interactions. Of course, this is impossible to verify by means of fitting or simulating the magnetic susceptibility data due to the large size of the cluster.

In order to establish the ground state for **1** variable temperature and variable field dc magnetization data were collected in the ranges 2-7 K and 0.5-7 T However, no satisfactory fit of the data was possible employing a model that assumes only the ground state is populated, possibly due

to the presence of the Gd^{III} ions mediating weak exchange interactions.

Given the large remaining magnetic moment for both clusters at low temperature and the lack of a superposition of the reduced magnetization (*RM*) *versus* *H*/*T* data on a single master curve (Figure S3), especially for **2**, suggest the presence of a moderate magnetic anisotropy and/or low-lying excited states, and therefore *ac* magnetic susceptibility measurements were performed on polycrystalline samples of **1** and **2** in the 1.8-8 K range in zero applied dc field and a 3.5 G ac field oscillating at 200-1000 Hz. For complex **2** the in-phase signal decreases upon decreasing temperature, indicating the presence of low-lying excited states with larger "*S*" values than the ground-state (Figure 4, top), while in addition frequency-dependent out-of-phase (χ_M'') signals, almost fully-formed, are observed below ~4.5 K (Figure 4, bottom), suggesting possible single molecule magnetism behaviour. On the contrary, complex **1** displays no out-of-phase signals.

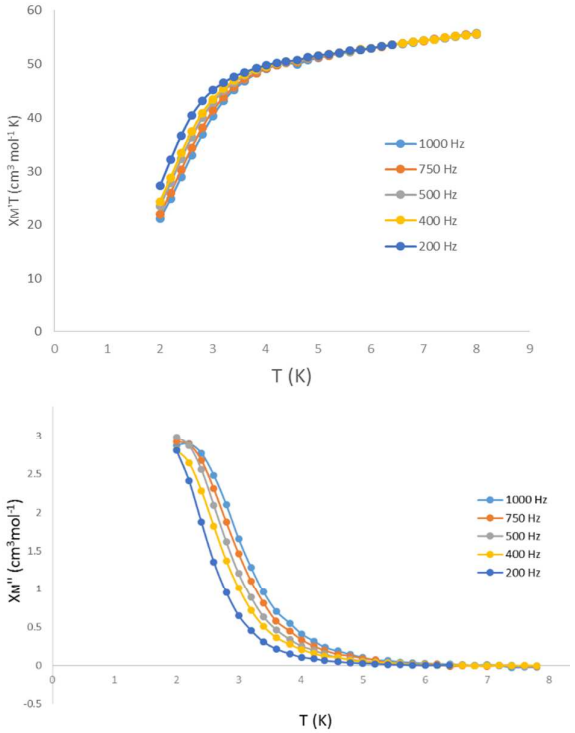


Figure 4. Plot of the in-phase χ_M'T (top) and out-of-phase χ_M'' signals (bottom) for **2** in ac susceptibility studies vs. *T* in a 3.5 G oscillating field at the indicated frequencies.

Complexes **1** and **2** join a very restricted family of [Mn6Ln6] complexes, comprising cluster $[Mn^{III}_4Mn^{IV}_2Dy_6(H_2shi)_4(Hshi)_2(shi)_{10}(MeOH)_{10}(H_2O)_2]\cdot 9MeOH\cdot 8H_2O$ (H_3shi= salicylhydroxamic acid) which also functions as a SMM,[10] and cluster $[Mn^{II}_6Dy_6(OH)_2(O_3PCH_2Ph)_6(O_2C^tBu)_{16}]\cdot 5MeCN$,[11] while **1** and **2** are the first examples containing exclusively trivalent manganese ions.

Conclusions

In conclusion, two new heterometallic dodecanuclear $[Mn^{III}_6Ln_6]$ (Ln = Gd, Dy) clusters were synthesized by the use of the H_3L (= 2-(β-naphthalideneamino)-2-hydroxymethyl-1-propanol) ligand in mixed-metal manganese-lanthanide carboxylate cluster chemistry, and their magnetic properties were studied, revealing possible single molecule magnetism behaviour for the Dy analogue. Furthermore, clusters **1** and **2** represent elegant examples of how a small change in a reaction can affect the identity of the products, since in the absence of carboxylate ligands octanuclear $[Mn^{III}_6Ln^{III}_2]$ species were obtained.[5]

Acknowledgements

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Notes and references

§ Crystal data for **1**: $C_{195}H_{190.50}Gd_6Mn_6N_{14.50}O_{57}$, M = 4922.25, triclinic, space group P-1, a = 18.252 (6) Å, b = 19.702 (7) Å, c = 31.519 (10) Å, α = 82.74 (4)°, β = 78.67 (4)°, γ = 65.87 (4)°, V = 10129 (7) $Å^3$, Z = 2, T = 80 K, R1 (I > 2σ) = 0.11 and wR2 (all data) = 0.291 for 67341 reflections collected, 18007 observed reflections (I > 2σ(I)) of 41988 (Rint = 0.082) unique reflections and 2145 parameters, GOF = 1.05. CCDC reference number: 1063249.

1 See for example: G. Aromi and E. K. Brechin, *Struct. Bonding*, 2006, **122**, 1; R. Bircher, G. Chaboussant, C. Dobe, H. U. Güdel, S. T. Ochsenbein, A. Sieber and O. Waldman, *Adv. Funct. Mater.*, 2006, **16**, 209; D. Gatteschi and R. Sessoli, *Angew. Chem., Int. Ed.*, 2003, **42**, 268; G. Christou, D. Gatteschi, D. N. Hendrickson, and R. Sessoli, *MRS Bull.*, 2000, **25**, 66; C. J. Milios and R. E. P. Winpenny, *Struct. Bond.*, 2015, **164**, 1; D. N. Woodruff and R. E. P. Winpenny, R. A. Layfield, *Chem. Rev.* 2013, **113**, 5110; P. Zhang, Y.-N. Guo and J. Tang, *Coord. Chem. Rev.*, 2013, **257**, 1728; H. L. C. Feltham and S. Brooker, *Coord. Chem. Rev.*, 2014, **276**, 1; J. D. Rinehart and J. R. Long, *Chem. Sci.*, 2011, **2**, 2078; N. Magnani, *Int. J. Quantum Chem*., 2014, **114**, 755; P. Zhang, L. Zhang and J. Tang, *Dalton Trans.*, 2015,**44**, 3923; C.-I. Yang, Z.-Z. Zhang and S.-B. Lin, *Coord. Chem. Rev.*, 2015, **289**, 289.

2 Representative refs and refs therein: A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M. G. Pini and M. A. Novak, *Angew. Chem., Int. Ed.*, 2001, **40**, 1760; R. Clérac, H. Miyasaka, M. Yamashita and C. Coulon, *J. Am. Chem. Soc*., 2002, **124**, 12837; L. Bogani, A. Vindigni, R. Sessoli and D. Gatteschi, *J. Mater. Chem*., 2008, **18**, 4750; C. Coulon, H. Miyasaka and R. Clérac, *Struct. Bonding*, 2006, **122**, 163; H. Miyasaka and M. Yamashita, *Dalton Trans*., 2007, 399; H.-L. Suna, Z.-M. Wang and S. Gao, *Coord. Chem. Rev*., 2010, **254**, 1081; W.-X. Zhang, R. Ishikawa, B. Breedlove and M. Yamashita, *RSC Adv*., 2013, **3**, 3772; D. Gatteschi and A. Vindigni, *Molecular Magnets* in "Nanoscience and Technology" book series, Eds. J. Bartolomé, J. F. Fernández and F. Luis, Springer-Verlag: Berlin Heidelberg, 2014; C. Coulon, Vivien Pianet and R. Clérac, *Struct. Bonding*, 2015, **164**, 143; R. Lescouëzec, J. Vaissermann, C. Ruiz-Pérez, F. Lloret, R. Carrasco, M. Julve, M. Verdaguer, Y. Dromzee, D. Gatteschi and W. Wernsdorfer, *Angew. Chem. Int. Ed.*, 2003, **42**, 1483; H.

Miyasaka, M. Julve, M. Yamashita and R. Clérac, *Inorg. Chem.*, 2009, **48**, 3420; J. Ferrando-Soria, D. Cangussu, M. Eslava, Y. Journaux, R. Lescouëzec, M. Julve, F. Lloret, J. Pasán, C. Ruiz-Pérez, E. Lhotel, C. Paulsen and E. Pardo, *Chem. Eur. J.*, 2011, **17**, 12482; T. Liu, H. Zheng, S. Kang, Y. Shiota, S. Hayami, M. Mito, O. Sato, K. Yoshizawa, S. Kanegawa and C. Duan, *Nat. Commun.* 2013, **4**, 2826.

3 C. P. Rao, A. Sreedhara, P. V. Rao, B. M. Verghese, E. Kolehmainen, N. K. Lokanath, M. A. Sridhar and J. S. Prasad, *J. Chem. Soc., Dalton Trans.* 1998, 2383.

4 A. B. Canaj, D. I. Tzimopoulos, A. Philippidis, G. E. Kostakis and C. J. Milios, *Inorg. Chem.*, 2012, **51**, 10461.

5 T. G. Tziotzi, D. A. Kalofolias, D. I. Tzimopoulos, M. Siczek, T. Lis, R. Inglis and C. J. Milios, *Dalton Trans*., 2015, **44**, 6082.

6 R. A. Coxall, S. G. Harris, D. K. Henderson, S. Parsons, P. A.Tasker and R. E. P. Winpenny, *J. Chem. Soc, Dalton Trans*., 2000, 2349.

7 I. D. Brown and D. Altermatt, *Acta Crystallogr.*, *B*, 1985, **41**, 244; H.H. Thorpe, *Inorg. Chem*., 1992, **31**, 1585.

8 A. W. Addison, T. N, Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.,* 1984, 1349.

9 M. Llunell, D. Casanova, J. Girera, P. Alemany and S. Alvarez, SHAPE, version 2.0, Barcelona, Spain 2010.

10 C. M. Zaleski, E. C. Depperman, J. W. Kampf, M. L. Kirk and V. L. Pecoraro, *Angew. Chem. Int. Ed.,* 2004, **43**, 3912.

11 Y.-Z. Zheng, E. M. Pineda, M. Helliwell and R. E. P. Winpenny, *Chem. Eur. J.*, 2012, **18**, 4161.

Two dodecametallic heteronuclear manganese-lanthanide [$Mn^{III}_6Ln^{III}_6$] (Ln= Gd, Dy) complexes were isolated and characterized by magnetic measurements.